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FOR MORE INFORMATION
Anatoly I. Frenkel
Physics Department
Yeshiva University
Anatoly.Frenkel@yu.edu

SIZE-CONTROLLED SYNTHESIS AND CHARACTERIZATION OF THIOL-STABILIZED GOLD NANOPARTICLES

A.I. Frenkel[1], S. Nemzer[1], I. Pister[1], L. Soussan[1], T. Harris[1], Y. Sun[1], and M.H. Rafailovich[2]

[1]Yeshiva University; [2]Stony Brook University

We synthesized thiol-protected gold nanoparticles by varying just one parameter: the gold-thiol ratio (ξ), within the range from 6:1 to 1:6. Their size and structure were analyzed self-consistently using transmission electron microscopy to measure their size distribution and EXAFS to measure their coordination numbers and nearest-neighbor distances. Surface tension in the framework of the spherical drop model was used to interpret apparent bond length shortening as ξ decreased. The smallest of such particles (16 Å in diameter) were obtained for ξ = 1:1 and the average size did not change as ξ was lowered to 1:6. We interpret this behavior in terms of surfactant-mediated stabilization of the particle size.

Size-controlled synthesis of nanoparticles less than a few nanometers in diameter is a challenge due to the spatial resolution limit of most scattering and imaging techniques used for their structural characterization. We present a self-consistent analysis of the extended x-ray absorption fine-structure (EXAFS) spectroscopy data of ligand-stabilized metal nanoclusters. Our method employs the measurement of the coordination numbers and metal-metal bond-length decrease that can be correlated with the average diameter and structure of the nanoparticles in the framework of the surface tension model and different structural motifs. To test the method, we synthesized and analyzed a series of dodecanethiol-stabilized gold nanoparticles where the only control parameter was the gold/thiol ratio ξ, varied between 6:1 and 1:6.

The dodecanethiolate gold nanoparticles were synthesized by the Brust method at the undergraduate chemistry laboratory of Yeshiva University's Stern College for Women. They were analyzed by transmission electron microscopy at the National Science Foundation Garcia Materials Research Science and Engineering Center at Stony Brook University. EXAFS data were collected at NSLS beamline X16C. It is evident that the particle size is reduced by lowering the Au/thiol ratio as inferred from the visible changes in the relative contributions of Au-Au and Au-S bonds to the Au L_3 EXAFS (**Figure 1A**). The contributions of the Au-Au or Au-S interactions to EXAFS progressively become less important, or more important, respectively, as ξ decreases. Indeed, the particle size decrease lowers the amplitude of Au-Au EXAFS oscillations due to the truncation effect (atoms on the surface of the particle are surrounded by fewer neighbors than those in the bulk and, hence, the average coordination numbers of Au-Au decrease) and enhances the amplitude of Au-S EXAFS due to the larger surface/bulk ratio.

Authors (from left) M. Rafailovich, A. Frenkel, I. Pister, L. Soussan, S. Nemzer, and T. Harris

EXAFS data were analyzed by fitting FEFF6 paths to Au-S and Au-Au shells. The particle diameters can be estimated, among other methods, by assuming specific polyhedral shapes that Au nanoparticles can adopt: The icosahedral, cuboctahedral, and truncated octahedral are among the most commonly discussed geometries. In our case, the cuboctahedral fcc model was chosen due to the similarity between the nanoparticles data and bulk Au data (**Figure 1A**) for all ξ. The particle diameters were obtained from their Au-Au coordination numbers (**Figure 2**).

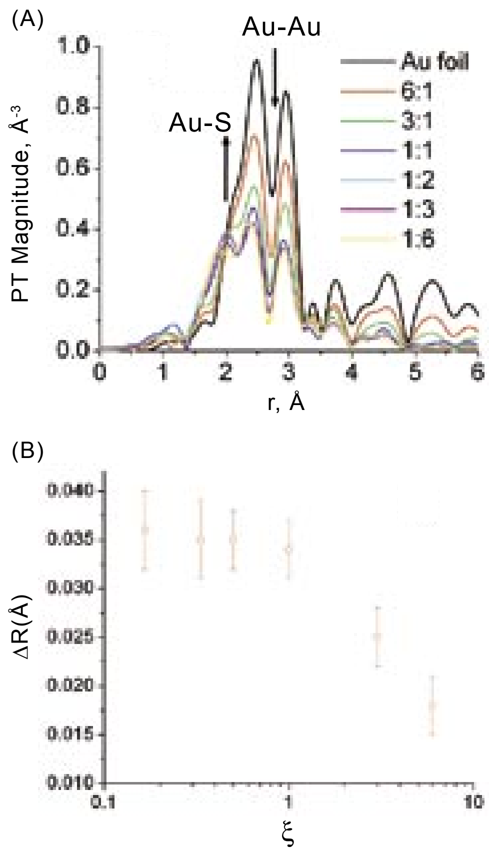
For all samples, the second quantity, $\Delta R(\xi) = R_0 - R(\xi)$, where R_0 = 2.88 Å in bulk gold and $R(\xi)$ is the bond length measured at the certain ξ, monotonically as ξ increases (**Figure 1B**). Such 1NN distance shortening at smaller sizes has a familiar ring from the lattice contraction of closely packed nanoparticles that has been previously interpreted in terms of surface stress by Mays, et al. (1968) using electron microscopy. We relate the particle diameter *d* to the relative lattice contraction $\alpha = \Delta R/R$ via the surface stress and compressibility *K*:

$$d = \frac{4}{3}\frac{f_{rr}K}{\alpha}$$

Using our EXAFS measurements of ΔR (**Figure 1b**) as well as the experimentally determined values for *K* and f_{rr}, we obtained the particle diameters for all ξ (**Figure 2**). The fact that both (independent) techniques of EXAFS data analysis that we employed for the particle diameter determination (by using the coordination numbers and the distance contraction) obtain very similar results (**Figure 2**) characterizes these results as highly reliable.

Our results for the gold-core sizes obtained by the new EXAFS analysis procedure are in good agreement with Scherrer analysis and statistical thermodynamic calculations by Leff, et al., which find that the thiol-capped gold nanoparticles should reach the minimum size of 14.7 ± 3.7 Å for a certain Au/thiol ratio (ξ_0) beyond which, for $\xi < \xi_0$, the thiols will be present in solution as monomers instead of assembling on the nanoparticle surface. In our work, a similar result (the gold-core size stabilizes at its minimum value of 16 ± 2 Å at $\xi_0 \approx 1:1$) was obtained by two independent methods of EXAFS analysis: the coordination number method and the surface tension method in the framework of the spherical drop model.

In summary, the size and structure of thiol-coated gold nanoparticles can be controlled by a single parameter: the Au/thiol ratio. We demonstrated that their lattice contraction follows the simplified spherical drop model and their size stabilization at the lowest Au/thiol ratio can be explained by the interplay between Au-thiol and thiol-thiol interactions.



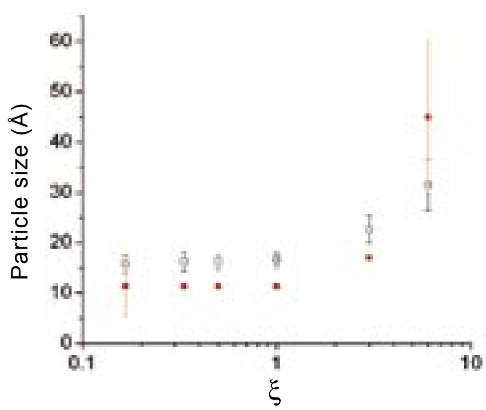


Figure 1. Particle size decrease and saturation is evidenced in EXAFS data of the samples prepared by the two-phase method. (A) The coordination numbers of the Au-Au bonds decrease and for Au-S increase as ξ decreases. (B) Size-dependence of the average Au-Au distances (relative to the bulk) for the samples prepared by the two-phase method.

Figure 2. Particle sizes for the samples prepared by the Brust methods. The sizes were obtained by EXAFS using two analysis techniques: empty squares indicate the surface tension technique and filled circles were obtained from the coordination numbers characteristic for the cuboctahedral *fcc* packing.